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PROCESS EVALUATION - STEAM REFORMING
OF DIESEL FUEL OIL

by

George A. Jarvi
Ronald M. Bowman
Elias H. Camara
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3424 S. State Street
Chicago, Illinois 60616

24 December 1979

Final Technical Report for Phases I through IV - 24 April 1979 to 24 December 1979

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Prepared for

Electrical Power Laboratory
Electrochemical Division
U.S. Army Mobility Equipment Research and Development Command
Fort Belvoir, Virginia 22060

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PREFACE

This work was conducted for the U. S. Army Mobility Equipment Research and Development Command (MERADCOM), Fort Belvoir, Virginia, under Contract No. DAAK70-79-C-0048, "Process Evaluation - Steam Reforming of Diesel Fuel Oil." This program was conducted to further the development of phosphoric acid fuel cell power units, specifically, the fuel conditioning subsystem. Related programs sponsored by the U. S. Department of Energy include "Steam Reforming of No. 2 Fuel Oil," ERDA interagency E(49-48)-1020, Jet Propulsion Laboratory.¹ The Electric Power Research Institute (EPRI) has directed a study of high-temperature steam reforming of heavy fuels, EPRI Project RP1041-1, by Kinetics Technology International Corporation.²

We acknowledge Dr. Calvin H. Bartholomew of Brigham Young University for assistance in data interpretation, the staff of Xytel Corporation for help in design and construction of the equipment, and Mr. Peter A. Borzym and Mr. Marc Erlandson for assistance in carrying out the experimentation.

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EXECUTIVE SUMMARY

This project, "Process Evaluation — Steam Reforming of Diesel Fuel Oil," is an evaluation of a proprietary catalyst, LC-2, as a means of producing hydrogen-rich gas for use in a fuel cell power unit. The program is supported by the U. S. Army Mobility Equipment Research and Development Command (MERADCOM) under contract DAAK70-79-C-0048.

Hydrogen-rich gas was produced over a wide range of reaction conditions. This product gas contained small amounts of ethylene and benzene and may not be suitable for phosphoric acid fuel cells. Maximum hydrogen and minimum olefins and aromatics were produced at the most severe operating conditions attempted:

- 2000°F, mid-bed temperature
- H₂O/C mole ratio of 5
- 45 grams per hour fuel feed rate.

Theoretical complete conversion at these conditions indicates a production of 6.6 SCF/hr of hydrogen. A long-term duration test at these conditions produced over 3 SCF/hr of hydrogen. The test was terminated after 86 hours because a plug of carbon developed at the entrance to the catalyst bed.

The catalyst produces hydrogen in the presence of hydrogen sulfide. No naphthalene broke through the bed until oil amounting to 650 pounds per cubic foot of catalyst had passed through the bed.

Future work on the production of hydrogen from diesel fuel oil should include the following:

1. Additional catalyst development to decrease olefin and aromatic breakthrough
2. Prototype development to establish a system for vaporizing and mixing oil and steam without causing fouling upstream of the catalyst bed
3. Consideration of additional processes for modifying the feedstock before entering the catalyst bed, including hydrotreating or catalytic preheating.

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SECTION I

Introduction

The purpose of this project was to evaluate a catalyst, LC-2, for its capability of steam-reforming diesel fuel oil into a hydrogen-rich gas for use in fuel cell power units. As a logistic fuel, diesel oil will be available to mobile power units. Earlier work at IGT established that LC-2 will reform gasoline in the presence of sulfur. This study enlarges the scope of our previous work.

The criteria for successful steam reforming is not only the production of hydrogen but also the suitability of the product gas for phosphoric acid fuel cell feeds. The product must be low in aromatics and olefins that may be cumulative poisons. Methane and other hydrocarbons represent unconverted feed carbon. Carbon monoxide is a poison, but can be shifted.

Historically, steam reforming of diesel fuel oil has resulted in massive carbon deposition. This proceeds from thermal cracking at high temperature, carbon monoxide disproportionation, or condensation of aromatics. Naphthalene production can result from ethylene reactions or remain as unconverted feed. Were it possible, the problems of carbon deposition would be examined separately from those of catalyst activity and selectivity. In this study, we have tried to examine the catalyst in a realistic environment as free from system-caused carbon deposition as possible.

Phase 1 was devoted to planning the experimental program and designing the laboratory equipment. During Phase 2, the equipment was constructed and tested. Phase 3 was a series of experiments to determine the most favorable conditions for the long-term test, which was Phase 4. This final report covers the entire project, including the previously reported work and Phase 4.

SECTION II

Procedure

The objective of Phase 1 was to design the necessary equipment and to develop an experimental procedure. Fuel was purchased from an AMOCO retailer and characterized as required under Fed. Spec. VV-F-800B grade DF-2 at IGT and at Phoenix Chemical Laboratory. Table 1 lists the specific tests from Fed. Spec. VV-F-800B, which we performed without variation from the text of the specification. The alternative ASTM methods listed in Table 2 were used for some tests rather than the methods recommended in Fed. Spec. VV-F-800B for the reasons stated in the table. Table 3 lists tests that we felt critical to the proper conduct of the evaluation, but that are not specified in Fed. Spec. VV-F-800B.

Deionized water was used for steam generation. Water for use in the evaluation was drawn from a fresh deionizing cartridge and stored in sufficient quantity for the experiments. Considering the ultimate application to a field power-generation facility, this water was much purer than what will be encountered in the field. However, at this point, we are concerned with the performance of the catalyst free from the effect of water impurities.

The condensible fraction in the reaction products was cooled and collected in a knock-out pot during steady-state operation. The breakthrough of reactant oil through the catalyst bed was estimated by separating the condensable fraction.

The product-gas analysis was performed by gas chromatography and mass spectrometry. Hydrogen content of certain runs was determined by a Carle gas chromatograph. Samples from other runs were analyzed with a Hewlett Packard 5700 thermal-conductivity chromatograph to determine the concentration of methane through propylene. Complete gas-product compositions were determined by mass spectrometry.

The most favorable process conditions of temperature, volume hourly space velocity of oil, and steam-to-carbon atom ratio were determined in a series of 6- to 8-hour experiments by varying either temperature, steam to carbon ratio, or space velocity while holding the other two variables constant. Overnight, the reactor was steamed at low flow and 1700°F.

Table 1. ASTM METHODS FOR DIESEL FUEL OIL FROM FED. SPEC. VV-F-800B

Test Item	ASTM No.	Standard
Cloud point	D 2500	*
Pour point	D 97	*
Distillation	D 86	90% @ 357°C, max e.p. @ 371°C, max
Water & Sediment	D 2709 & D 2273	0.01%, max
Accelerated Stability	D 2274	1.5 mg/100 mil, max
Neutralization	D 974	0.10 TAN, max
Particulate Contamination	D 2276	8.0 mg/liter, max
Cetane number	D 976	45, min **
Ash	D 482	1 wt %, max

* Fed. Spec. VV-F-800B does not specify limits for these items per se: "... the maximum limit must be specified by the procuring activity." Item in question will be reported.

** Appendix II of Fed. Spec. VV-F-800B contains a method for determining whether cetane improvers are present. After the determination is made that none are present, D 976 will be used to calculate cetane index. Mr. Arnold Parus, AMOCO, indicates that nitrogen cetane improvers are not routinely used in this area.

Table 2. EXCEPTIONS TO ASTM METHODS RECOMMENDED IN FED. SPEC. VV-F-800B

Test Item	Recommended Method	IGT Method	Reason	Standard
Specific Gravity	D 287	D 1298	(a)	32.9 to 41.0 °API
Flash Point	D 93	E 134	(b)	56°C, min
Kinematic Viscosity	D 445	D 88	(b)	1.9 to 9.5 c St
Carbon Residue	D 524	D 189	(b)	0.20 wt % max on 10% bottoms
Sulfur Content	D 1552	D 2622	(b), (c)	0.70 wt %, max

(a) Method held to be fastest and sufficiently accurate.

(b) Materials at hand for substitute test, which is sufficiently accurate.

(c) D 2622 is an alternate method listed in VV-F-800B

Table 3. TESTS REQUIRED FOR MASS BALANCE
NOT CALLED FOR IN FED. SPEC. VV-F-800B

Test Item	Method
Carbon	D 3178
Hydrogen	D 3178
Nitrogen	D 271**
Oxygen	By Difference
Sulfur	*
Ash	*
Moisture	*
Sulfur Species in Feed Oil	GC-Mass Spec.
Sulfur Species in Product Gas	GC-Flame Photometric
Sulfur Species in Product Liq.	GC-Mass Spec.
Ammonia in Product Gas	Ion-Selective Electrode
Ammonia in Product Liq.	Ion-Selective Electrode

* These are specified in VV-F-800B.

** Nitrogen and ammonia tests called for by reason of fuel cell degradation.

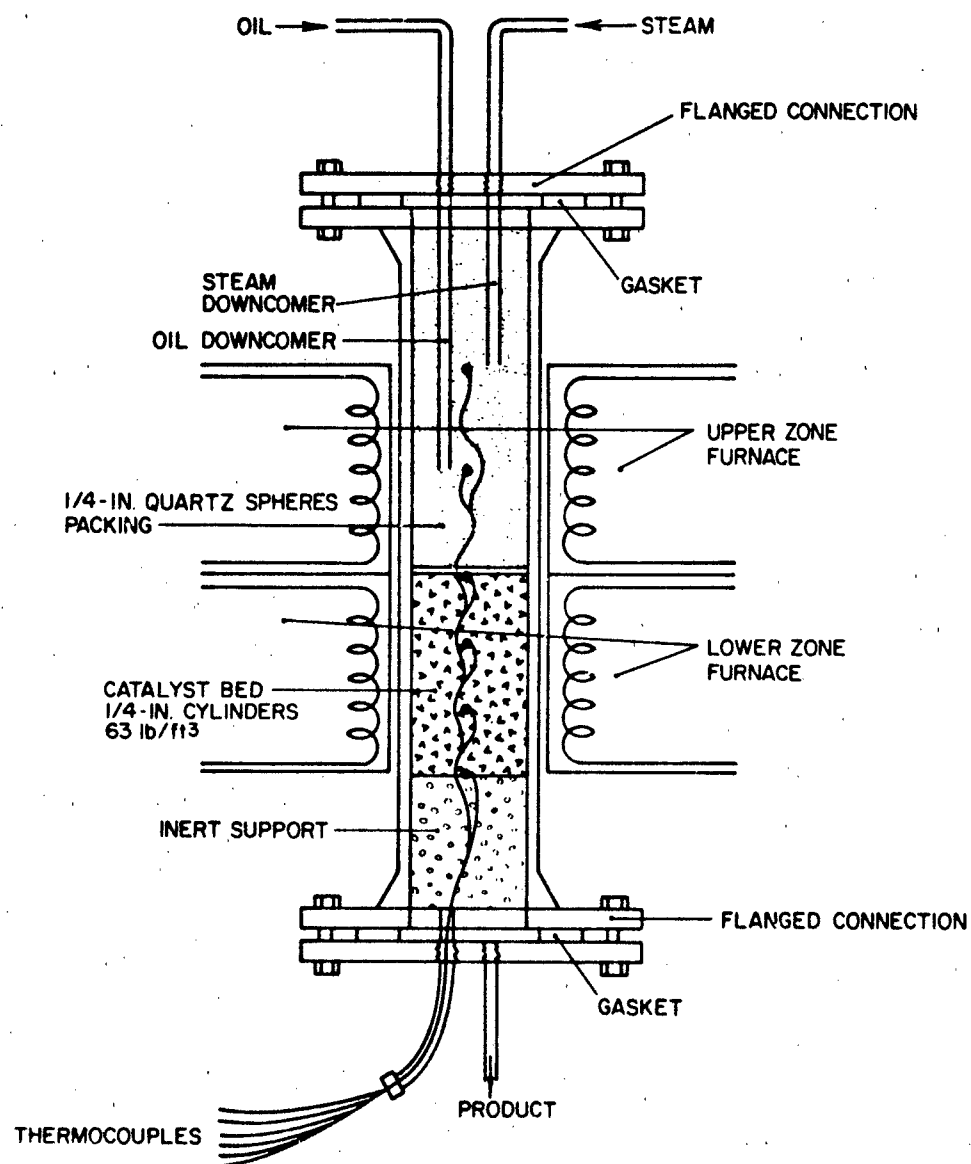
The concentration of hydrogen in the product stream constituted the criterion for the selection of process conditions. The rates of production of other gases, such as methane, carbon monoxide, olefins, and aromatics, were also considered because of their potential impact on fuel cell performance and system efficiency.

Apparatus

The reactor used for parametric testing was a packed-bed tube reactor made of Schedule 40 Rolled Alloy 330 pipe with flanged connections, as shown in Figures 1, 2, and 3.

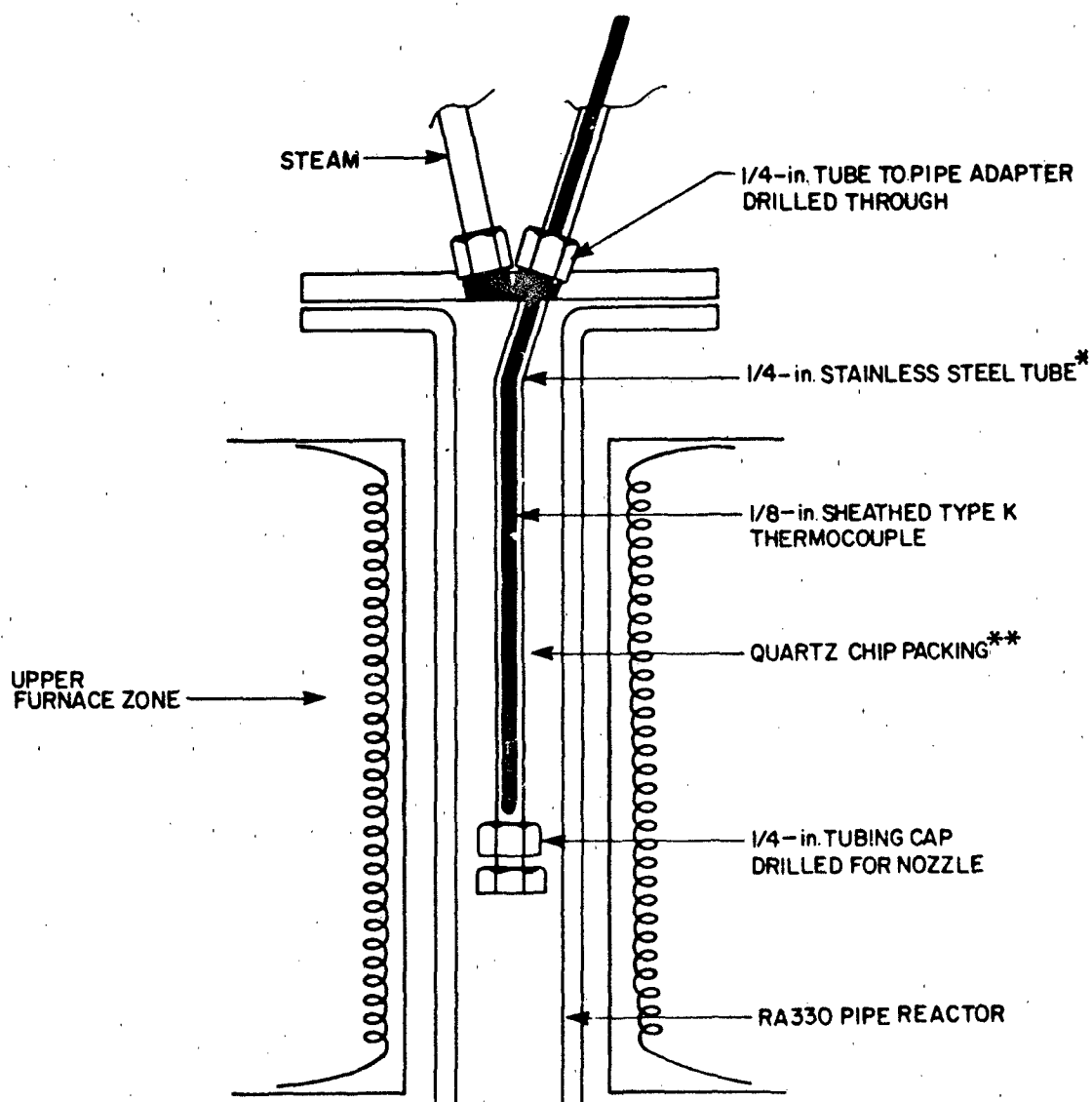
The following items were considered in the design of the reactor:

- Temperature. The reactor was constructed of materials which tolerate temperatures of 1800°F.
- Pressure. The contract for this evaluation specified "essentially atmospheric" conditions.
- Materials of Construction. Rolled Alloy 330 was used for the reactor because stainless steel is susceptible to fatigue at high temperatures.



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Figure 1. STEAM REFORMING REACTOR — PRELIMINARY DESIGN

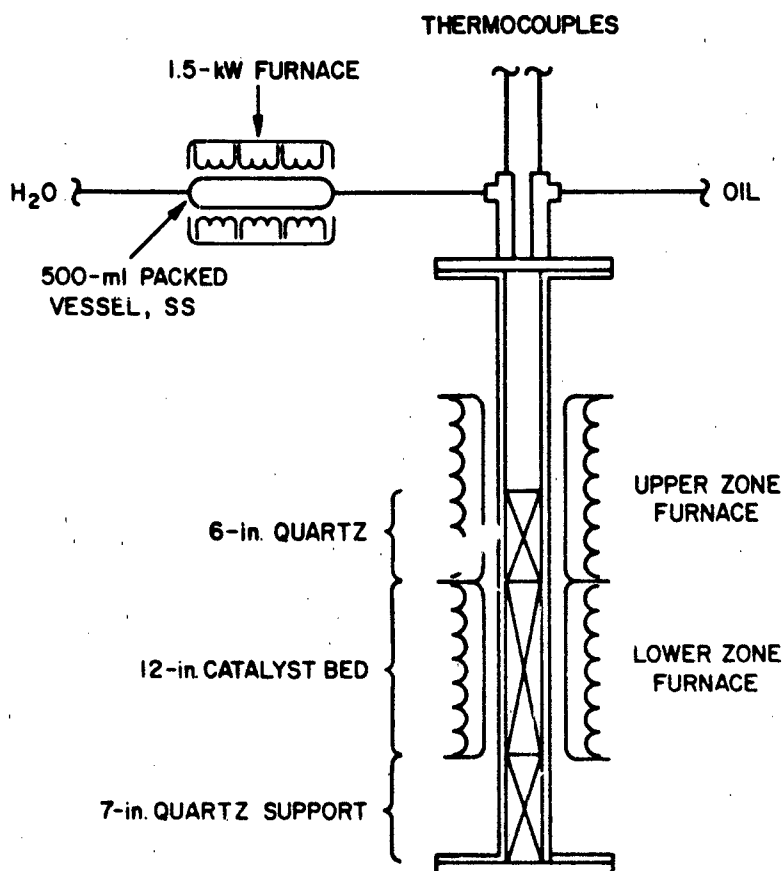


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Figure 2. STEAM REFORMING REACTOR - SECOND DESIGN

* Oil flows in annulus between 1/4-in. tube and 1/8-in. thermocouple.

** Steam flows in annulus between 1/4-in. tube and reactor.



- NOTE:
1. H_2O VAPORIZES IN VESSEL PACKED WITH STAINLESS STEEL WOOL, INSIDE THREE 500-WATT OVENS.
 2. H_2O AND OIL TEMPERATURES ARE MONITORED AT THE UPPER FLANGE.
 3. H_2O VAPOR MOVES SLOWLY THROUGH UPPER ZONE WHILE HOT OIL FALLS THROUGH TO QUARTZ BED.

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Figure 3. STEAM REFORMING REACTOR — FINAL DESIGN

- d. Closure. A butt-welded flange was used with a Flexitallic seal style CF-1C, made of 316 stainless steel and asbestos. The flange was located far enough from the furnace hot zone to allow the use of stainless steel. Flange and gasket assembly were pressure-tested to 100 psig at room temperature.
- e. Geometry. The oven for the reactor had an inside diameter large enough to accommodate 1-inch Schedule 40 pipe. This was large enough to avoid channeling effects around catalyst pellets and small enough to minimize radial heat transfer effects. Considering the flow rate of steam and space velocity of oil, a catalyst bed of 12-inch depth was selected. An additional 12 inches of length in the oven was used for a vaporization and mixing zone.
- f. Instrumentation. The total system included means of determining temperature, pressure, water and oil flow rates. External to the apparatus, means for gas analysis, liquid analysis, and calibration of the system instruments were available.

Four Inconel sheathed thermocouples were used to establish the axial temperature profile through the catalyst bed. A sleeve and Conax fitting was installed on the flange to introduce the .040-inch diameter thermocouples into the reactor vessel.

Pressure was indicated on a 0-100 psi gauge located so as to monitor the reaction-zone pressure. Water and oil flow rates were metered by means of a constant displacement pump for each fluid, calibrated gravimetrically. Alarm monitors were provided for high temperature.

- g. Reactor Internals. Based on our previous experience with reforming AMOCO gasoline, and also with hydrogasifying diesel fuel oil, we attempted to vaporize the oil and mix it with superheated steam within the reactor vessel upstream of the catalyst bed, as shown in Figure 1.

Initially, the vaporization zone was loaded with quartz chips that provide excellent high-temperature stability, low internal surface area, and adequate external surface for oil vaporization. Heat transfer characteristics of quartz are marginal, but are sufficient for the process.

The main objective in choosing these reactor internals and oven sizes was to prevent local conditions of carbon formation within the catalyst bed. The overall stoichiometry does not promote carbon formation. But if unvaporized oil is allowed to contact the catalyst pellets, or if liquid rather than vapor water contacts the oil, allowing the oil to exist at relatively long residence times in liquid or vapor state at high temperature, the local thermodynamic criteria for coke formation are satisfied. On several occasions, carbon did deposit on the catalyst bed, requiring modification of the reactor packing scheme. Figures 1, 2, and 3 give the different configurations used during the evaluation. Figure 3 is the configuration used for the bulk of the Phase 3 testing and the long-term test.

A process flow diagram is shown in Figure 4. There are two feed lines, an inert purge line, and one product stream. The product stream contains a knock-out pot to separate the condensibles from the gas product. Liquid can be drawn off from the knock-out pot periodically, such as at the beginning and end of a steady-state experiment.

Water and oil are pumped into the system as liquids, and preheated by line heaters. The filtering, calibration, and pressure relief systems for both streams are similar. Liquid is stored in vessels blanketed with inert gas.

The reaction products are separated at nearly atmospheric conditions. The product gas is either vented or sampled for gas chromatography. As much as 2% to 3% of the gas product passing on to the dry test meter will be water vapor at these conditions.

The valves and instruments called out in Figure 4 are specified in Table 4.

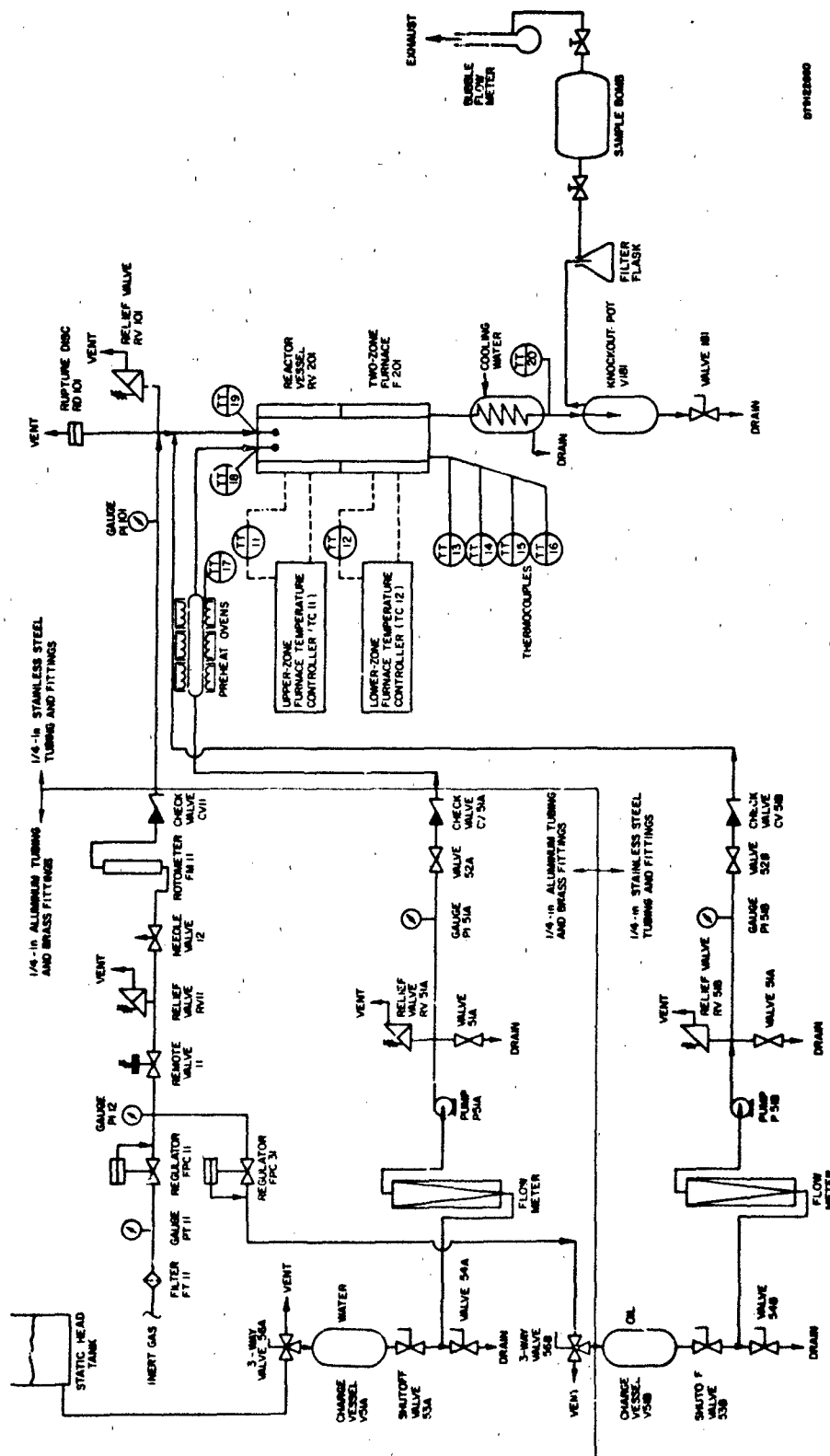


Figure 4. REVISED PROCESS FLOW DIAGRAM FOR STEAM REFORMING

Table 4. EQUIPMENT LIST FOR STEAM REFORMING SYSTEM

Item	Code	Make	Model No.
Filter	FT11	Whitey, 7 micron	B-4TF-7
Gauge	PI11	Wika, 0-3000 psig	CO-1014
Regulator	FPC11	Tescom, 0-100 psi	44-2262-241
Gauge	PI12	Wika, 0-100 psig	CO-1004
Gauge	PI51A	Wika, 0-100 psig	CO-1004
Valve	11	Whitey, pneumatic	B-92S4
Regulator	FPC31	Tescom, 0-15 psi	101-3004-2
Relief Valve	RV11	Nupro, 100 psig	B-4CA-50
Relief Valve	RV51A	Nupro, 100 psig	B-4CA-50
Rotameter	FM11	Labcrest	FP-1/8-09-6-3
Check Valve	CV11	Nupro, 10 psi cracking	SS-4C-10
3-way Valve	56A	Whitey	B-42XS4
3-way Valve	57A	Whitey	B-42XS4
Valve	53A	Whitey	B-42S4
Valve	54A	Whitey	B-42S4
Valve	55A	Whitey	B-42S4
Pump	P51A	Fluid Metering 150-1500 cc/hr	RP-SY-2SSY
Pump	P51B	Fluid Metering 30-300 cc/hr	RP-G20-1SSY
Valve	51A	Whitey, regulating	B-1RS4-A
Valve	52A	Whitey, regulating	B-1KS4
Check Valve	CV51A	Nupro, 1/3 psi cracking	SS-4C-1/3
Check Valve	CV51B	Nupro, 1/3 psi cracking	SS-4C-1/3
Check Valve	CV81	Nupro, 1/3 psi cracking	SS-4C-1/3
3-way Valve	56B	Whitey	SS-42XS4
3-way Valve	57B	Whitey	SS-42XS4
Valve	53B	Whitey	SS-42S4
Valve	54B	Whitey	SS-42S4
Valve	55B	Whitey	SS-42S4
Relief Valve	RV51B	Nupro, 100 psig	SS-4CA-50
Relief Valve	RV101	Nupro, 100 psig	SS-4CA-50
Valve	51B	Whitey, regulating	SS-1KS4-A
Valve	52B	Whitey, regulating	SS-1VS4
Gauge	PI51B	Wika, 0-100 psig	CO-2304
Gauge	PI101	HTL, 0-100 psig 1/4"	101F-4 1/2-100
Rupture Disc	RD101	BS and B	77-24-0547-23
Upper Zone Controller	TC202	Barber-Colman	528Z-4-0030-054-0-47
Lower Zone Controller	TC202	Barber-Colman	528Z-4-0030-054-0-47
Knock-out Pot	V101	Whitey, 1 gal.	304-HDF8-1 gal.
Valve	181	Whitey	SS-1KM4
Relief Valve	RV81	Circle Seal, 4 psi set	532T-2MP-4
Two Zone Furnace	F201	ATS, 24", 2.7 kW	3210
Temperature Indicator	DTI	Metermaster 0-1999°F	AN2572-X-I-P-X-K-F
Selector Switch		Omega	OSW3-12
Temperature Alarm Module	TAM	Actionpak	AP-1200-2357-6

SECTION III

Results

A 7-gallon sample of diesel oil was purchased from an AMOCO retailer. The results of analyses required for Federal Specification VV-F-800B, Symbol DF-2 certification are listed in Table 5. Additional analyses required for mass balances are shown in Table 6 and the aromatic compounds present in the fuel, including sulfur-containing species, are listed in Table 7. The sulfur in the aromatic compounds is 0.21 weight percent and accounts for 86% of the total sulfur.

Table 5. ANALYSIS OF DIESEL FUEL OIL (Per Fed. Spec. VV-F-800B)

Test	Test ASTM Designa- tion	Result	Standard for DF-2
Gravity	D 1298	34.5° API	32.9 to 41.0
Flash Point	E 134	147°F	133°F, min
Cloud Point	D 2500	- 2°F	9°F, max
Pour Point	D 97	- 30°F	0°F, max
Kinematic Viscosity	D 88	37.8 SUS (3.6 cSt)	1.8 to 9.5 cSt
Distillation	D 86	50% - 482°F 90% - 600°F e.p. - 614°F	50% - report 90% - 675°F, max e.p. - 700°F, max
Carbon Residue	D 189	0.00 wt %	0.20 wt %, max on 10% bottoms
Sulfur	D 2622	0.25 wt %	0.7 wt %, max
Copper Strip Corrosion	D 130	1A	1
Ash	D 482	0.00 wt %	0.02 wt %, max
Water and Sediment	D 2709 D 2273	0.00 wt %	0.01 wt %, max
Accelerated Stability	D 2274	1.3 mg/100 ml	1.5 mg/100 ml, max
Neutralization	D 974	0.06 mg KOH/g	0.10 mg KOH/g, max
Particulate Contamination	D 2276	1.3 mg/l	8 mg/l, max
Cetane Number	D 976	44.5	45, min

Table 6. ULTIMATE ANALYSIS OF DIESEL FUEL OIL

Element	Dry Basis wt %
Carbon	87.03
Hydrogen	12.64
Sulfur	0.25
Nitrogen	0.08
Ash	0.00

Table 7. AROMATIC AND SULFUR-CONTAINING AROMATIC COMPOUNDS
IN DIESEL FUEL OIL

Compound Class	Formula	Weight Percentage
Ethylbenzene/Xylenes	C_8H_{10}	0.28
C ₃ -benzenes	C_9H_{12}	1.00
C ₄ -benzenes	$C_{10}H_{14}$	1.12
Indan	C_9H_{10}	0.17
Naphthalene	$C_{10}H_8$	0.73
Methyl naphthalenes	$C_{11}H_{10}$	3.02
C ₂ -naphthalenes	$C_{12}H_{12}$	4.68
C ₃ -naphthalenes	$C_{13}H_{14}$	2.33
Biphenyl	$C_{12}H_{10}$	1.47
Methyl biphenyl	$C_{13}H_{12}$	0.04
Aceraphthene	$C_{12}H_{10}$	0.11
Diphenylmethane	$C_{13}H_{12}$	0.16
Diphenylethane	$C_{14}H_{14}$	0.35
Fluorene	$C_{13}H_{10}$	0.26
Phenanthrene	$C_{14}H_{10}$	0.39
Anthracene	$C_{14}H_{10}$	0.01
C ₅ -thiophene	C_9SH_{14}	0.01
Methylbenzothiophenes	C_9SH_8	0.02
C ₂ -benzothiophenes	$C_{10}SH_{10}$	0.15
C ₃ -benzothiophenes	$C_{11}SH_{12}$	0.26
C ₄ -benzothiophenes	$C_{12}SH_{14}$	0.28
Dibenzothiophene	$C_{12}SH_8$	0.12
Methyl dibenzothiophenes	$C_{13}SH_{10}$	0.23
C ₂ -dibenzothiophenes	$C_{14}SH_{12}$	0.25
Unidentified aromatics		12.9
Total aromatics		30.3

The data gathered in Phase 3 are summarized in Tables 8 and 9. Table 8 gives the operating conditions along with the product analysis. Table 9 gives the hydrogen-conversion results as a function of temperature, space velocity, and steam-to-carbon ratio, grouped accordingly.

These data are plotted parametrically in Figures 5, 6, and 7. There are distinct trends of increased hydrogen conversion with increasing temperature and decreasing space velocity. The slight trend of increased hydrogen conversion with increasing steam-to-carbon ratio may or may not be significant, considering the adverse trade-off with increased water consumption.

The effect of increased severity is pronounced over the range of conditions studied. The maximum conversion was obtained at 2050°F, the greatest temperature the reactor materials can withstand, and at 45 g/hr, the lowest

Table 8. EXPERIM

Run No.	1	2	3	4	5	6	7	8	9	10
Catalyst Volume, cc	170	170	170	170	170	170	170	170	170	170
Catalyst Bed Depth, in.	12	12	12	12	12	12	12	12	12	12
Catalyst Weight, gram	236.9	221.9	221.9	221.9	221.9	241.5	241.5	241.5	226.8	226.8
Time Catalyst on Stream, hr	45	34	66	27	112	24	24	72	22	74
Time Catalyst on Oil, hr	2	2	2	2	2-1/2	5-2	4	6	2	4
Pressure at top of Bed, psig	2.5	1.5	5.0	1.5	5.0	5.5	4.5	2.0	2.5	2.5
Temperature, °F	1490	1002	450	240	500					
(TC Depth, inches)	(1")	(1" above)	(1" above)	(1" above)	(1" above)	1196	1080	1414	1293	1260
	1480	1480	1420	1109	1370	(3")	(3")	(3")	(4")	(4")
	(4")	(4")	(4")	(4")	(4")	1645	1575	1705	1660	1710
	1660	1781	1580	1713	1720	(7")	(7")	(7")	(8")	(8")
	(8")	(8")	(8")	(8")	(8")	1775	1747	1836	1880	1825
	600	1015	902	1157	1210	(12")	(12")	(12")	(-1")	(-1")
Diesel Flow Rate, g/hour	(3" below)	(1" below)	(1" below)	(1" below)	(1" below)	127.8	174.6	73.2	91.8	102.1
Water Flow Rate, g/hour	94.0	73.2	72.6	61.2	117.0	994.2	1,383.8	577.2	660	660
Steam/Fuel Weight Ratio	508	575	588	642	912	7.78	7.81	7.86	6.54	5.88
Hydrocarbon Conversion, %	6.1	7.3	8.1	10.5	7.8	5.96	6.04	5.01	4.51	4.51
Diesel Space Velocity, hr ⁻¹	4.68	6.02	6.20	8.03	5.97	129	170	74	73	103
Diesel Space Velocity, hr ⁻¹	92	74	73	62	118					
Product Gas Composition, mole %										
Air (Free)	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1
Hydrogen Sulfide	0.0	0.0	0.0	0.0	0.0	0.03	0.01	0.01	0.02	0.01
Nitrogen	0.3	0.1	0.3	0.3	0.3	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	16.0	14.3	6.2	10.1	17.4	15.7	6.0	11.2	15.2	12.2
Oxygen	2.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Dioxide	50-60	11.9	14.5	11.9	11.4	9.6	3.3	10.7	9.7	9.2
Hydrogen	49.7	49.4	53.6	53.9	45.1	29.6	49.6	30.6	43.5	43.5
Argon	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Helium	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methane	7.0	9.7	9.4	7.8	7.1	10.3	15.7	11.0	9.7	12.3
Ethane	0.4	0.8	0.7	0.2	0.6	1.2	0.4	0.6	0.4	0.4
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-Butane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
i-Butane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pentanes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hexanes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Heptanes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Octanes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethylene	5.0	10.1	10.3	8.9	6.4	13.8	24.0	12.1	11.5	13.4
Propylene	1.0	1.3	2.8	2.2	0.9	2.2	5.4	1.5	1.4	1.9
Butenes	0.1	0.4	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pentenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hexenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Heptenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Octadiene	0.7	1.3	1.0	0.6	1.2	3.2	0.7	0.5	0.5	0.5
Pentadiene	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.0	0.0
Cyclopentadiene	0.2	0.3	0.2	0.2	0.2	1.6	0.2	0.1	0.1	0.1
Acetylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-Propadiene	0.0	0.1	0.1	0.1	0.2	0.3	1.3	0.2	0.2	0.4
Benzenes	1.9	3.2	2.3	0.7	1.6	2.9	0.8	0.3	0.3	2.7
Toluenes	0.3	0.9	0.7	0.2	0.5	0.7	0.2	0.1	0.1	0.8
Xylenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethyl Benzenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Styrenes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Product Gas Flow Rate, SCF/hr	4.48	1.1	2.45	5.32	3.72	7.42	6.42	5.23	6.51	6.4
Product Gas Yield, SCF/lbm	22.10	11.80	16.40	29.47	22.20	26.40	16.70	32.44	32.20	28.8
Product Gas Space - Time Yield, hr ⁻¹	780	855	442	887	953	1,237	1,070	872	1,085	1,017
Liquid Hydrocarbons, gram/hour	440	10	4	2.2	12	35	17	13	17	17
Hydrogen Conversion Fraction	7.23	8.35	4.22	8.45	4.37	6.34	1.63	6.47	10.08	8.42
(H ₂ Produced / H ₂ O Feed + 2H in Oil)										
Hydrocarbon Conversion, %	402	851	952	962	952	912	882	772	842	872

^a SCF of all vapor on C₁₀H₂₂ per cubic foot of catalyst time per hour.

^b Standard relative to 60°F, 1 atm (dry basis).

^c SCF gas produced per cubic foot of catalyst time per hour.

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EXPERIMENTAL DATA

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Table 9. HYDROGEN CONVERSION RELATIVE TO TEMPERATURE, SPACE, VELOCITY, AND H₂O/C RATIO

Run No.	Temperature, °F	H ₂ O/C Ratio	Oil Feed, gram/hour	Gas Product, SCF/lbm	% H ₂	H ₂ Conversion *
Effect of Varying Temperature						
2	1781	6.02	73.2	31.8	49.7	8.35%
3	1580	6.20	72.6	16.6	49.4	4.22
8	1705	6.04	73.2	32.4	49.6	8.47
10	1710	4.51	102.0	28.8	43.5	8.48
11	1801	4.50	102.0	38.9	50.5	13.31
17	1750	5.53	60.1	25.6	44.1	6.42
18	2050	5.53	60.1	67.1	55.2	21.07
19	2050	4.46	60.2	48.9	55.5	18.53
20	1750	4.46	60.2	16.0	37.5	4.10
21	2050	4.50	45.0	48.7	59.6	19.42
22	1750	4.50	45.0	18.8	45.1	5.66
Effect of Varying Space Velocity						
2	1781	6.02	73.2	31.8	49.7	8.35%
5	1730	5.97	117.0	22.2	53.9	6.37%
6	1645	5.96	129.0	26.4	45.1	6.34
7	1575	5.98	175.0	16.7	29.6	2.63
19	2050	4.46	60.2	48.9	55.5	18.53
21	2050	4.50	45.0	48.7	59.6	19.42
20	1756	4.46	60.2	16.7	37.5	4.10
22	1750	4.50	45.0	18.8	45.1	5.66
Effect of Varying H ₂ O/C Ratio						
8	1705	6.04	73.2	32.4	49.6	8.47%
9	1660	5.01	91.8	32.2	50.6	10.08
10	1710	4.51	102.0	28.8	43.5	8.48
13	1751	5.55	54.2	29.8	46.9	7.93
17	1750	5.53	60.1	25.6	44.1	6.42
14	1750	5.03	59.6	27.6	44.7	7.61
15	1756	4.47	59.7	24.6	41.5	6.96
20	1756	4.46	60.2	16.0	37.5	4.10
18	2050	5.53	60.1	67.1	55.2	21.07
19	2050	4.46	60.2	48.9	55.5	18.53

* H₂ produced per 2H fed as either H₂O or fuel hydrogen.

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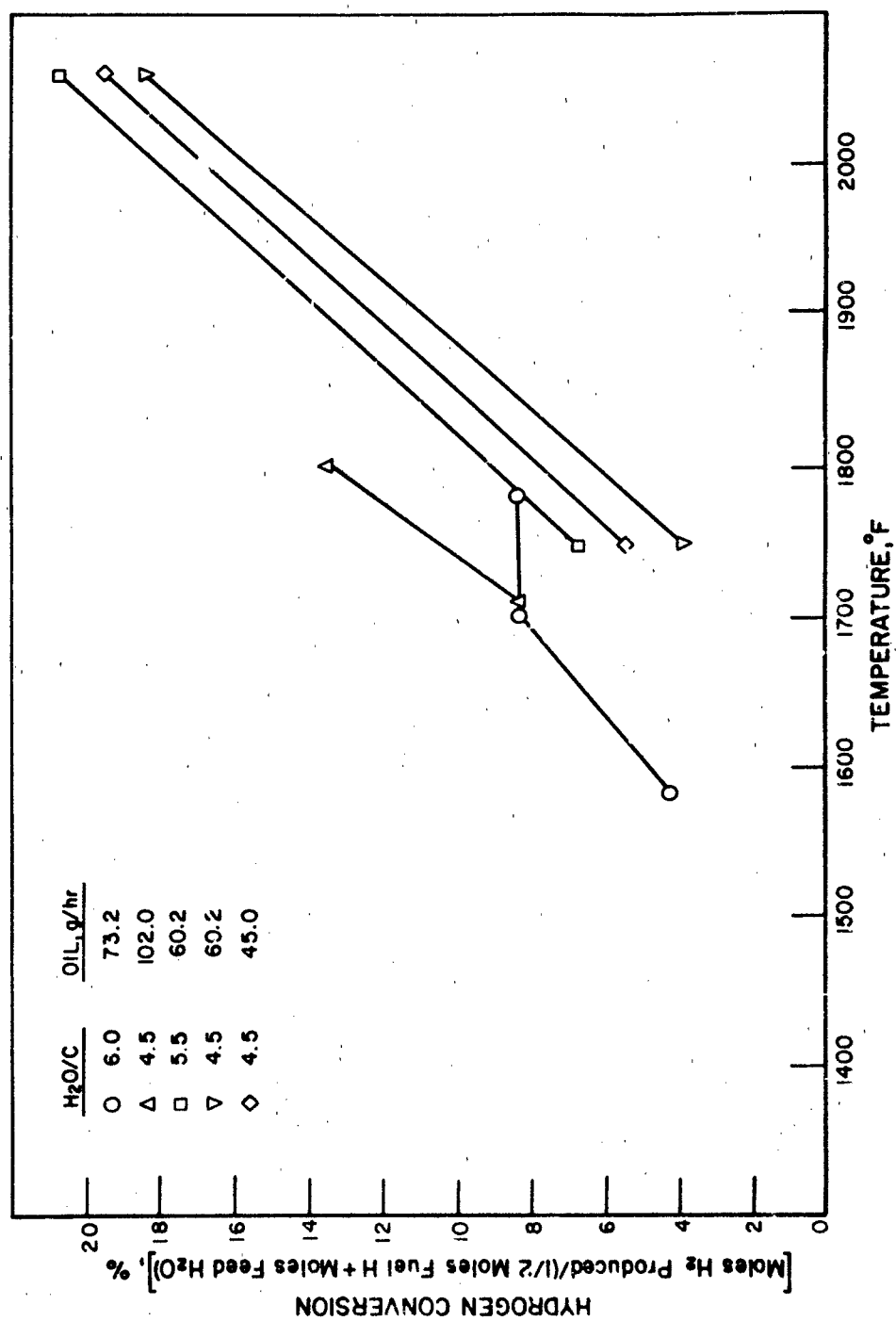
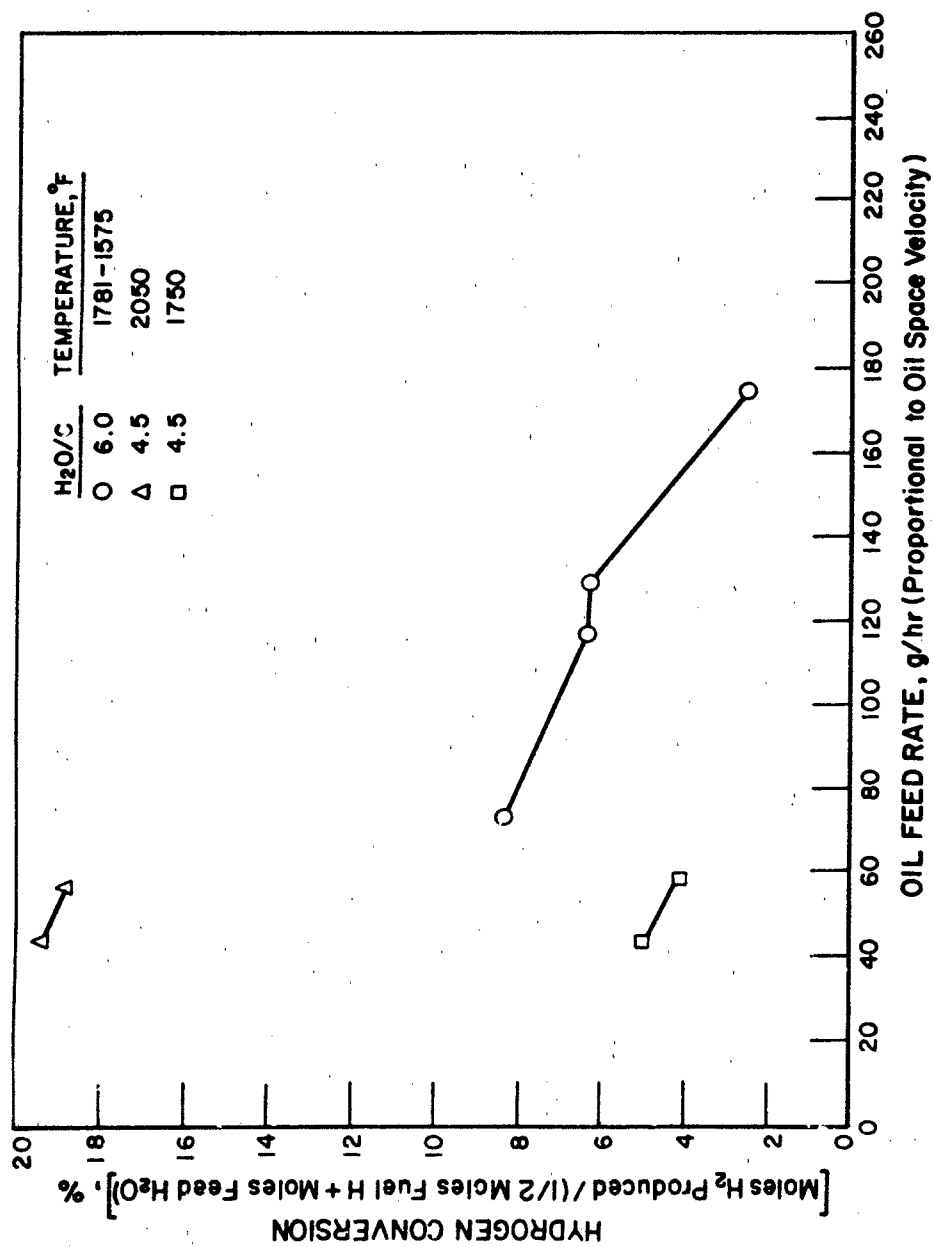
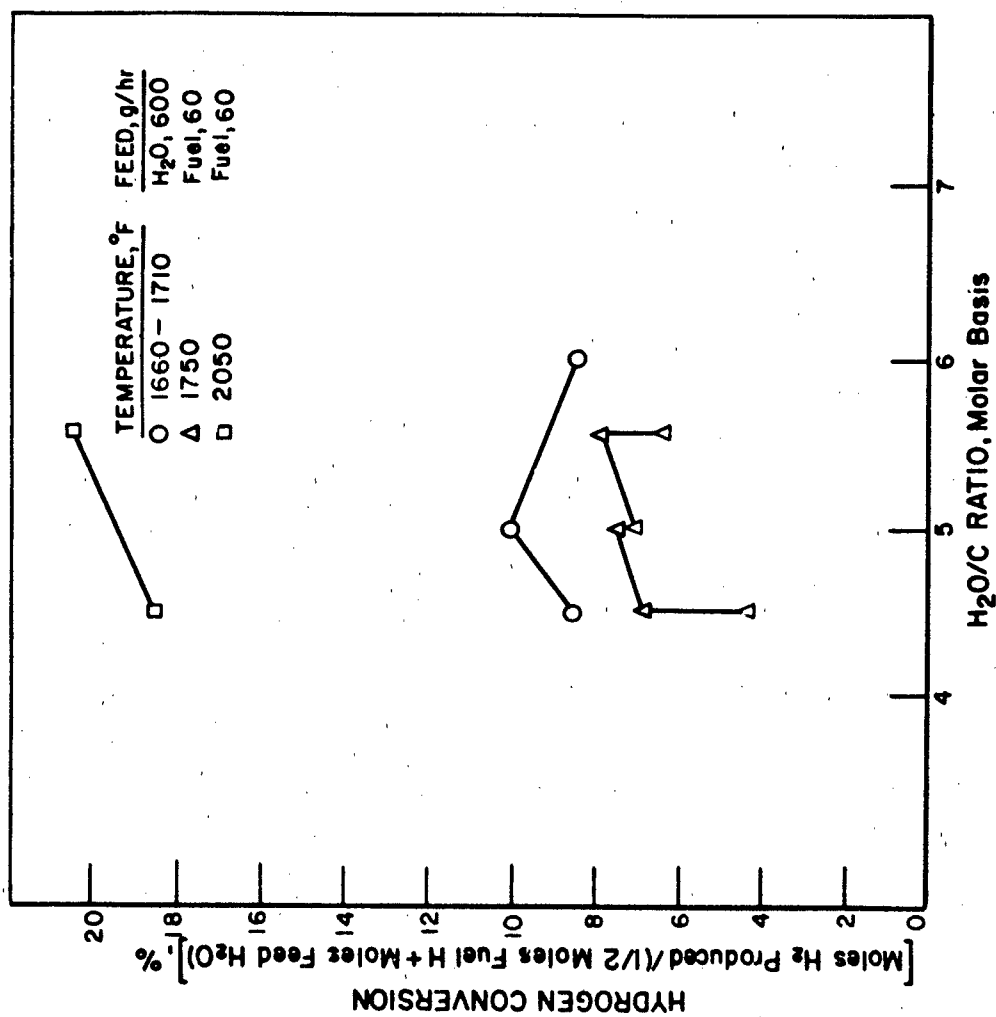


Figure 5. EFFECT OF TEMPERATURE ON HYDROGEN CONVERSION



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Figure 6. EFFECT OF OIL FLOW RATE ON HYDROGEN CONVERSION



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Figure 7. EFFECT OF H₂O/C RATIO ON HYDROGEN CONVERSION

flow rate the feed pump can provide. For these reasons, the operating conditions were selected at 2000°F and 45 grams oil per hour. The steam-to-carbon ratio was set at 5 moles of steam per gram-atom of carbon to provide sufficient water to inhibit carbon deposition but limit the water consumption.

The significance of hydrogen conversion must be interpreted in terms of suitability of the product gas for fuel cell use. Accordingly, ethylene, benzene, and methane product compositions have been plotted with respect to temperature in Figures 8, 9, and 10. Oil feed rate and H₂O/C ratio are given as parameters in these figures.

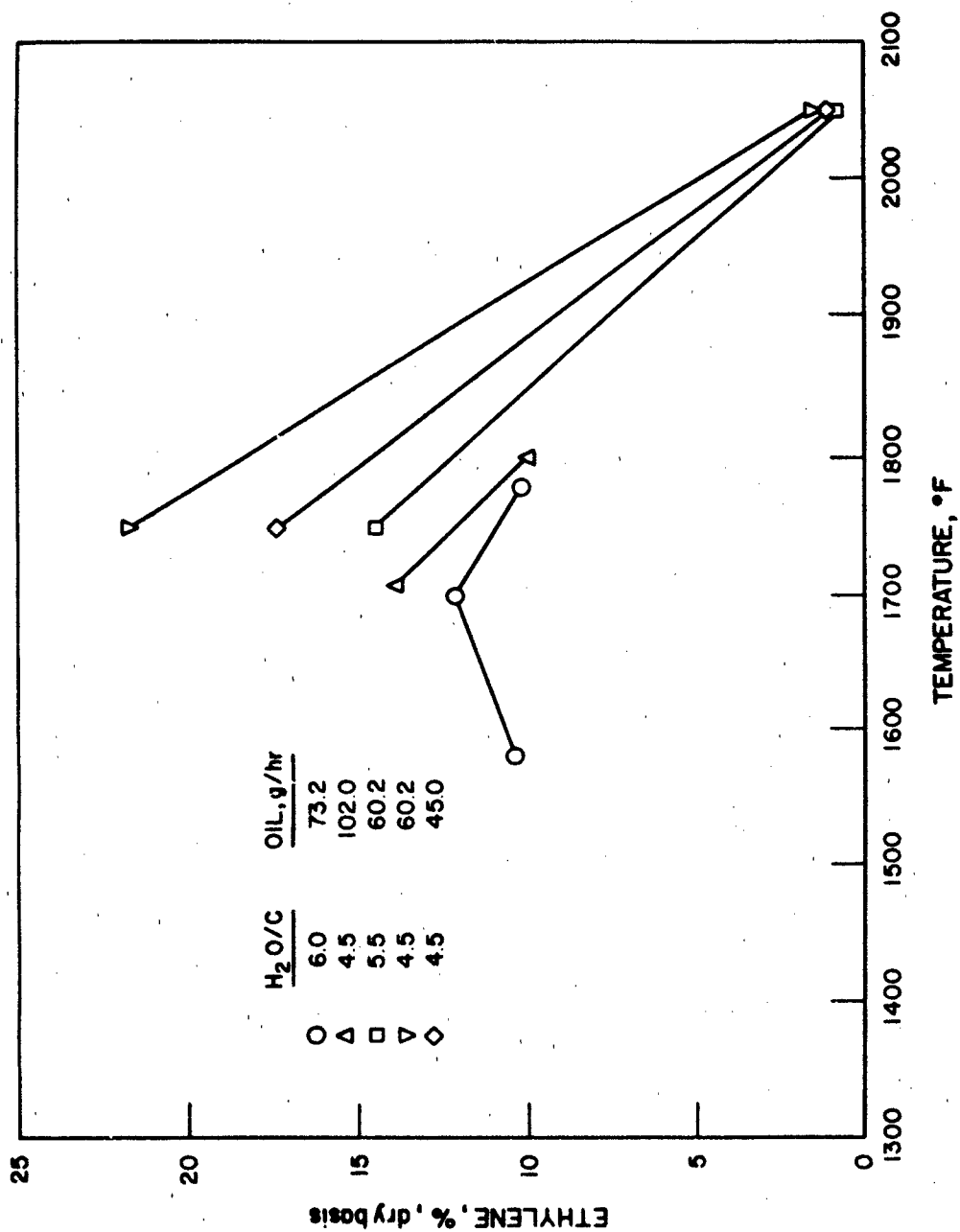
Ethylene, and all unsaturated hydrocarbons, must be reduced or eliminated for the application to phosphoric acid fuel cells. The trends discernible from Figure 8 are decreasing ethylene fraction with increasing temperature, decreasing space velocity, and increasing H₂O/C ratio. The same trends appear in Figure 9 for the benzene product fraction, and in Figure 10 for methane.

Other species appear in the mass spectrometry analysis of Table 8. Some, such as nitrogen, may be due to errors arising in the sampling procedure. Others, such as propylene or ethyl benzene, are minor and should be considered along with ethylene and benzene in an effort to tailor the product gas for use in a fuel cell stack.

Phase 4 experimentation consisted of one long-duration test of catalyst LC-2 at essentially atmospheric pressure, temperature of 2000°F, oil flow rate of 45 grams of oil per hour, and steam-to-carbon ratio of 5.0. The reactor was loaded to a depth of 12 inches of catalyst as in Figure 3. No inert gas diluent was employed during this or any other part of the evaluation. The operating conditions are summarized in Table 10.

The product-gas compositions for four gas samples are given in Table 11. Up to the time of termination, no significant decay in product-hydrogen concentration was observed. Therefore, the hydrogen concentration can be interpolated for the entire run and used to calculate hydrogen conversion and the production of hydrogen gas. The conversion and production data are both plotted in Figure 10.

The theoretical complete conversion of fuel to carbon monoxide would lead to the production of 6.55 SCF/hr of hydrogen gas. Due to reaction, kinetic, and



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Figure 8. EFFECT OF TEMPERATURE ON ETHYLENE PRODUCT FRACTION

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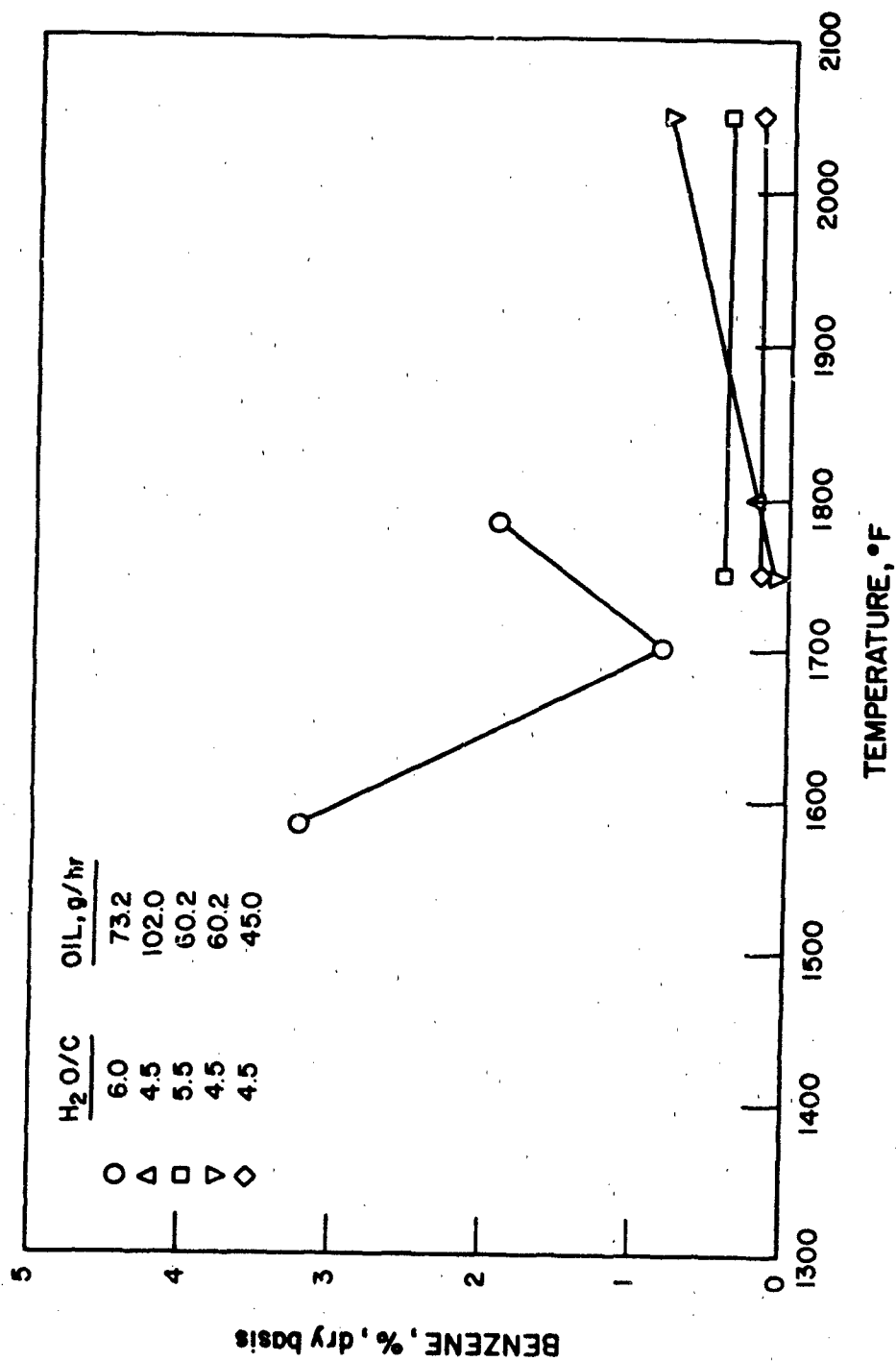
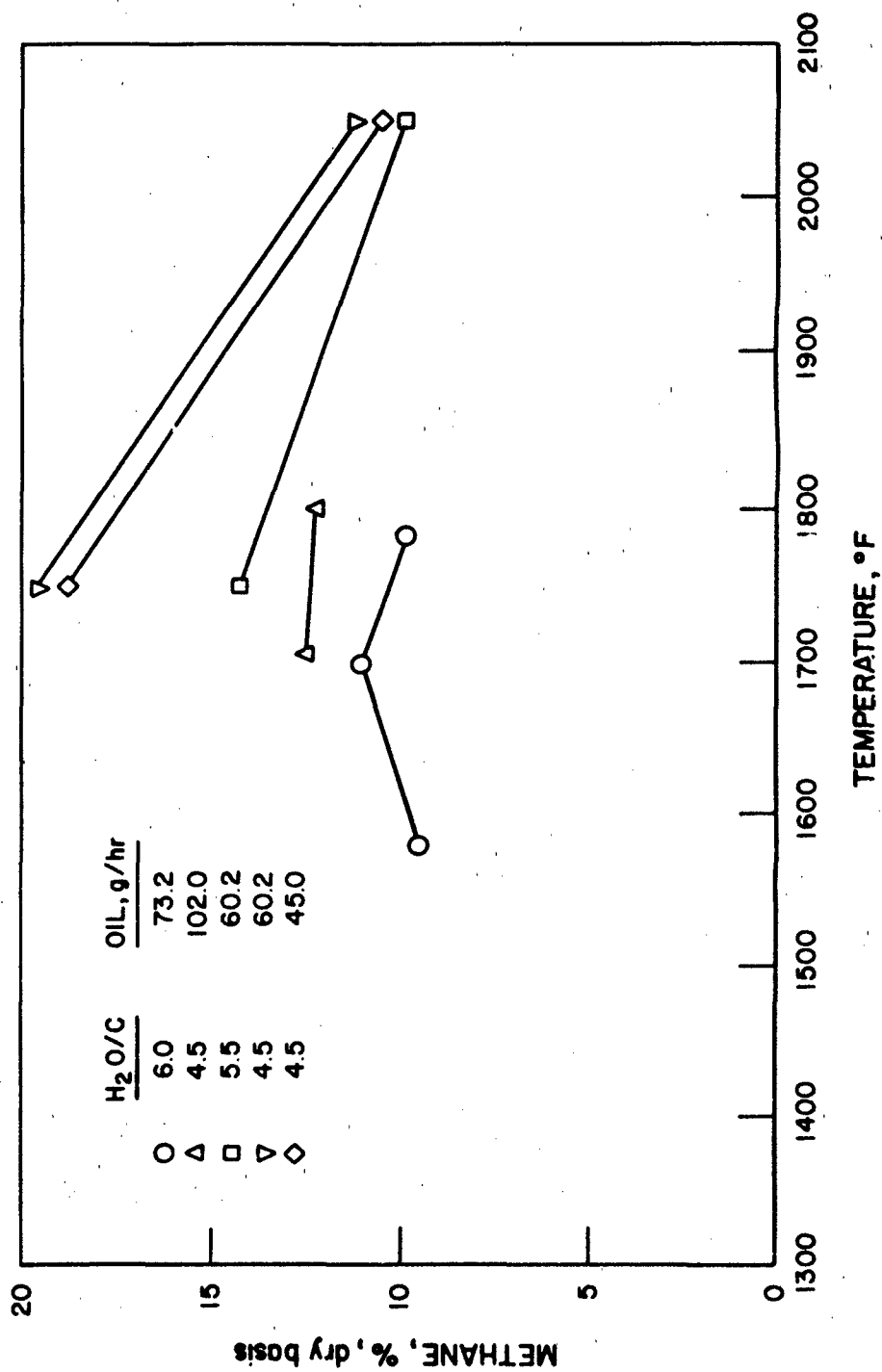


Figure 9. EFFECT OF TEMPERATURE ON BENZENE PRODUCT FRACTION



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Figure 10. EFFECT OF TEMPERATURE ON METHANE PRODUCT FRACTION

Table 10. PHASE 4 LONG-TERM DURATION TEST CONDITIONS

Catalyst Volume	170 cm ³ (10.4 in ³)
Catalyst Weight	235 g (0.52 lbm)
Bed Depth	30.5 cm (12 in)
Diesel Oil Feed Rate	44 g/hour (0.10 lbm/hour)
H ₂ O Feed Rate	290 g/hour (0.64 lbm/hour)
Steam/Fuel Weight Ratio	6.64
H ₂ O/C Mole:Atom Ratio	5.08
Diesel Weight Velocity	45 lbm fuel/(ft ³ of catalyst-hour)
Pressure (at top of bed)	0.4 to 5.0 psig
Temperature 1" above bed	880°C (1620°F)
4" into bed	1040°C (1900°F)
8" into bed	1090°C (1990°F)
1" below bed	260°C (500°F)

other limitations, only 5-1/2 SCF/hr of hydrogen were produced at the beginning of the experiment. After about 30 hours of operation, the rate of hydrogen production dropped to just over 3 SCF/hr. This rate remained relatively constant for the remainder of the experiment. The total product-gas flow rate during the experiment varied from 9 to 6 standard cubic feet per hour. The gas yield at the latter stages of the experiment was about 60 standard cubic feet per pound of oil fed to the process. The experiment ran 86 continuous hours until a pressure difference of 15 psi developed across the reaction, mainly during the last 5 hours.

Hydrogen conversion remained stable during the test, as did the concentration of hydrogen sulfide in the product gas. The reactor was cooled, opened, and examined for evidence of carbon deposition. The upper portion of the reactor near the entrance of the catalyst bed was obstructed, and the catalyst pellets were coated with a thin layer of either grey or black material.

Sulfur, as hydrogen sulfide and sulfur carbonyl, did in fact break through the catalyst bed. The analysis was performed in the lab via flame photometric gas chromatography. The batch of catalyst used for the test had previously been conditioned with steam and four hours of fuel at 1700°F. After 16 hours of operation at 1990°F, about 400 ppm H₂S and COS was detected in the product stream. The sulfur breakthrough was at about the same level 66 hours later. The entering fuel introduced sulfur at about 0.11 grams per hour. The product gas leaving the reactor contained about 0.10 ± 0.02 grams per hour. Therefore, the catalyst was sulfided, and steady-state hydrogenation of sulfur

was occurring. We have not established that failure resulted from sulfur poisoning, but we have established that hydrogen conversion was unaffected by steady-state breakthrough of sulfur.

Table 11. PRODUCT GAS COMPOSITIONS FROM PHASE 4 TEST

Run Time of Sample, hours	23	48	90	86
	Percentage, dry basis			
CO	14.9	16.3	17.3	15.5
CO ₂	13.4	13.9	11.9	14.1
H ₂	62.1	59.2	59.7	58.4
CH ₄	7.4	7.9	9.5	8.9
C ₂ H ₆	1.4	1.4	1.1	1.3
C ₆ H ₆	0.57	1.1	0.4	1.1
Toluene	0.04	0.1	0.0	0.1
Acetylene	0.01	0.0	0.0	0.0
Volume, parts per million				
H ₂ S	407			401

SECTION IV

Discussion

We have achieved the fundamental objective of evaluating catalyst LC-2 as a means of directly reforming diesel fuel oil, DF-2. The immediate finding of the Phase 4 long-term test is that the catalyst is prone to naphthalene breakthrough after 30 hours, but continues to produce hydrogen in the presence of hydrogen sulfide. The cause of carbon deposition in the entrance to the catalyst bed may be either catalyst or system-related phenomena.

Our major criteria in evaluating the results of the Phase 4 test are: First, does the catalyst produce hydrogen diesel oil continuously over the 200-hour period? Second, is the product gas of high quality for use in fuel cells? Third, can the low, "essentially atmospheric" pressure be maintained for the duration of the test? Fourth, does hydrogen sulfide break through the bed at a steady-state concentration?

First, the catalyst did produce hydrogen gas continuously throughout the test. Regardless of the other phenomena occurring in the system, the catalyst pellets unloaded after the test retained steam reforming activity.

Second, the product gas was not of fuel cell quality after about 50 hours of operation, although the level of ethylene, benzene, and other known phosphoric acid fuel cell poisons was lower than observed in Phase 3. During Phase 3 tests, fuel breakthrough was common. Very little fuel emerged during the first 30 hours of the Phase 4 test. At that point, naphthalene began to condense on the walls of the tubing leading from the reactor. This contributed to the pressure drop across the system. The production of naphthalene is unacceptable and the selectivity of catalyst LC-2 must be improved.

Third, at no time during the Phase 4 test did the pressure drop across the reactor exceed 20 psi. The pressure drop which developed at the 86th hour of the test was not a sudden increase in pressure. It was the last of a series of gradual increases in pressure, rising at about 1 psi per hour, which could not be relieved, as the others had been, by opening the reactor vent line and cleaning the tubing. After the test was terminated, the reactor was cooled as rapidly as possible without any flow of fuel, water, or purge gas. Carbonaceous material was observed at the top of the catalyst bed, suggesting that the flow restriction was caused by carbon deposition at that point.

The question remains as to whether the carbon deposition which ended the test resulted from sulfur poisoning of the upper portion of the catalyst bed. Chemical analysis of the spent catalyst is required to answer the question. If the solid material consists of condensed aromatics, then the catalyst may have been poisoned and, therefore, heavy, waxy hydrocarbon side-products built up a porous, semi-solid plug which solidified upon cooling. If the solid material consists of nearly pure carbon, then it could be that the steam reforming of the light hydrocarbon fraction occurred in the upper portion of the catalyst bed, and that carbon monoxide may have decomposed to solid carbon. The manufacturer is conducting the catalyst analysis.

Fourth, the rate of steam reforming for the Phase 4 test with steady-state breakthrough of hydrogen sulfide is evidence that catalyst LC-2 is active in the presence of reasonable levels of fuel sulfur.

In addition to the four criteria mentioned above, the amount of ammonia produced bears on the objective of evaluating the catalyst LC-2 for steam reforming of diesel fuel oil. Ammonia is undesirable in any amount in phosphoric acid fuel cells, yet it is reasonable to assume that the 0.04 grams per hour of fuel nitrogen are converted to ammonia. Fortunately, ammonia is soluble in the water phase. We estimate that if the water contained all the fuel nitrogen as ammonia, the concentration would be about 150 weight ppm, which is too low for our analytical department to detect inexpensively. If as much as a quarter of the ammonia produced resides in the gas phase, the concentration would be about 300 ppm or less in the product gas. Because we suspect that the gas concentration of ammonia is much less, no special equipment was purchased to confirm this estimate.

Although the approach to equilibrium is not one of the evaluation criteria, it is of value when comparing this study to past and future work. Assuming model compounds, free energy calculations predict that no carbon would survive at over 1700°F at 1 atmosphere as anything but carbon monoxide. Water, hydrogen, and the trace impurities would be produced strictly according to stoichiometry. However, in reality, we observed two items. First, the reaction did not proceed to equilibrium. Second, water-gas shifting of CO to CO₂ does occur to a significant extent downstream of the catalyst bed. While neither of these findings is particularly surprising, they do account for

the appearance of carbon dioxide, methane, and some of the other hydrocarbons. Although the program contract did not provide for a multi-catalyst bed, the utility of catalyst LC-2 could be enhanced with catalytic preheating in advance of the bed and by adjusting to a lower bed temperature to promote methane reforming.

SECTION V

Conclusions

We conclude from our investigation of catalyst LC-2 that although it does not reform diesel fuel oil, grade DF-2, Federal Specification VV-F-800B, into an acceptable phosphoric acid fuel cell fuel, it does accomplish the following:

- It maintains hydrogen conversion activity in the presence of hydrogen sulfide
- It delays naphthalene breakthrough until after 650 pounds oil per cubic foot of catalyst has passed through the bed
- It limits undesirable gas phase by-products to about 8% methane, 1-1/2% olefins, and 1% aromatics.

SECTION VI

Recommendations

We suggest the following three areas for future development:

- Basic catalyst studies to identify discrete failure modes. Catalyst characterization on the microscopic scale is required to determine the specific catalyst modifications that are needed.
- System integration studies. Other processes such as catalytic preheating or hydrotreating with product hydrogen recycle might produce a feedstock suitable for reforming. This is equivalent to revising the fuel specification.
- Catalyst modification. Funded or proprietary research may lead to the development of a catalyst more suitable for direct, high-temperature steam reforming of diesel fuel oil. The manufacturer of LC-2 has already produced a catalyst in order to reduce the amount of methane breakthrough.

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SECTION VIII

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2. Tio, R., Jones, R. and Minet, R., "Assessment of Fuel Processing Systems for Dispersed Fuel Cell Power Plants," EM-1010 Research Project 1041-1 Interim Report for the Electric Power Research Institute. Kinetics Technology International Corporation and Catalytica Associates, Inc., March 1979.

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APPENDIX. Marine Diesel Oil Test

A-1

I N S T I T U T E O F G A S T E C H N O L O G Y

APPENDIX

As reported earlier in a letter to MERADCOM dated December 27, 1979, an additional test was performed in conjunction with this diesel steam reforming process evaluation. A sample of "marine diesel oil" derived from oil shale was obtained from MERADCOM for use in a special test. The catalyst used for this test had been aged during Phase 3, having been cycled between daily reforming and overnight steaming for over 400 hours. In this manner, we observed hydrogen production without having to reload and condition batches of catalyst daily. The analysis of this fuel is given in Table A-1 and the run conditions are given in Table A-2.

The results of this test are given in Table A-3. At the conditions of this test, theoretical equilibrium predicts complete fuel conversion, but with a considerable amount of water remaining in the product. The results indicate that 11.2% of all the hydrogen entering the process leaves as hydrogen gas. This represents 35% of complete conversion of fuel to carbon monoxide.

Figure A-1 shows that the results of testing marine diesel oil over catalyst LC-2 are similar to the results of Phase 3 tests of No. 2 fuel oil. Therefore, we conclude that the marine diesel is comparable to fuel characterized as DF-2 in Fed. Spec. VV-F-800B, and that marine diesel may show comparable results at any of the operating conditions considered in this process evaluation.

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A-3

I N S T I T U T E O F G A S T E C H N O L O G Y

Table A-1. ANALYSIS OF SOHIO MARINE DIESEL

Carbon	86.7 wt %
Hydrogen	13.3 wt %
Nitrogen	0.01 wt %
Sulfur	0.002 wt %
Aromatics	29 vol %
Olefins	2 vol %
Saturates	69 vol %
Specific Gravity	0.835 grams/ml
Initial Boiling Point	398°F
50%	500°F
End Point	581°F

Table A-2. MARINE DIESEL STEAM REFORMING RUN CONDITIONS

Oil Feed Rate	59.9 grams per hour
Steam Feed Rate	399.3 gram per hour
Catalyst Loading, 12"	228.8 grams of "LC-2"
Centerline Bed Temperature	
above catalyst bed	~600°F
4" into catalyst bed	1470°F
8" into catalyst bed	1862°F
1" below bed	930°F
H ₂ O/C Ratio	5.12 $\frac{\text{moles H}_2\text{O}}{\text{g - atom}}$
Theoretical Total Conversion	6.55 SCF of H ₂ per hour relative to 0°C

Table A-3. MARINE DIESEL STEAM REFORMING TEST RESULTS

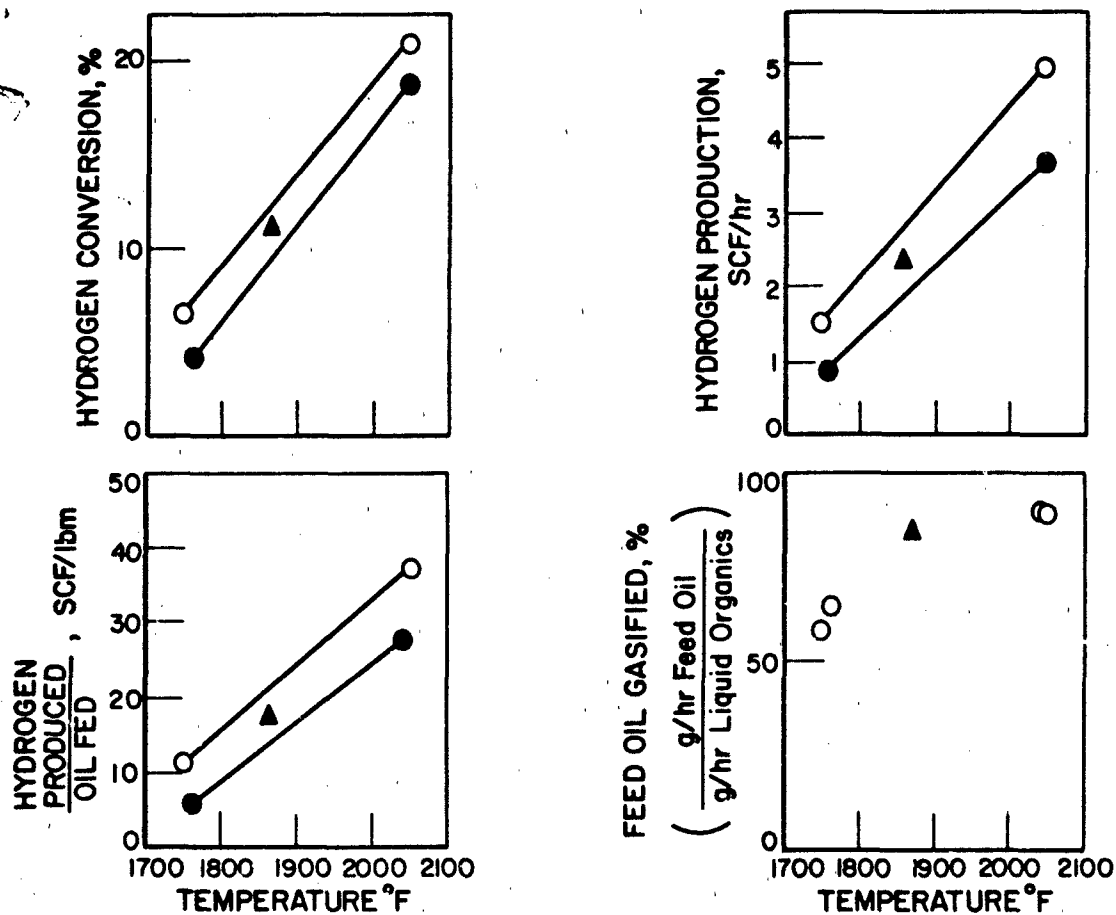
<u>Gas Product</u>	<u>Mole Percent</u>	<u>SCFH, dry basis, 0°C</u>
CO	17.3%	0.79
CO ₂	5.5	0.25
H ₂	50.4	2.31
CH ₄	12.7	.58
C ₂ H ₄	10.0	.46
C ₃ H ₆	0.2	.01
C ₂ H ₂	2.3	.11
C ₆ H ₆	0.6	.03
all other	0.7	.03
TOTAL	100.0	4.58 SCF/hour

Liquid Products, by difference

H ₂ O	328 gram/hour
Other condensible	9.4 gram/hour

Hydrogen Conversion 11.2% $\left(\frac{\text{moles H}_2 \times 100\%}{\text{mole H}_2\text{O fed} + 1/2 \text{ fuel H}} \right)$

Percent of Theoretical
Complete Conversion 35%



- DIESEL OIL $H_2O/C = 4.5$
 ● DIESEL OIL, $H_2O/C = 5.5$
 Δ MARINE DIESEL, OIL SHALE-DERIVED, $H_2O/C = 5.1$

ALL TESTS CONDUCTED AT 60g/hr FUEL FEED
 CATALYST VOLUME = 0.006 ft³

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Figure A-1. RESULTS OF SHALE-DERIVED MARINE DIESEL STEAM REFORMING TEST